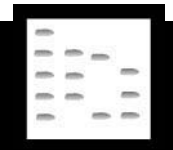
METAL ANALYSIS: GAS AND LIQUID CHROMATOGRAPHY



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Introduction

Since its inception as a separatory technique, gas–liquid chromatography (GLC) has had great impact in the quantitative resolution of mixtures of volatile compounds. Although the sister discipline of gas–solid chromatography (GSC) is used for inorganic gas analysis along with metalloid halides and hydrides, the potential of both GLC and GSC for inorganic compounds, metal complexes and organometallics has been less realized. The relative obscurity of inorganic gas chromatography derives from expectations that inorganic compounds are inherently of very low volatility and/or thermally unstable under GC conditions, are incompatible with column substrates, show undesirable reactivity making GC difficult, or are incompatible with conventional detectors. Some of these strictures apply, but there are many examples of GC of metallic and metalloid compounds including organometallics incorporating sigma or pi carbon to metal bonds, and metal complexes with coordinate bonds between oxygen, sulfur, nitrogen, phosphorus, or halogen, and the metal atom. Some metal oxides and halides may be eluted at high temperatures. Chemical derivatization methods may also enable successful elution. There is often considered to be a minimal group of chemical properties to be possessed by a compound before gas chromatography can be successful: volatility, thermal stability, monomeric form, neutrality, relatively low molecular weight, coordinative saturation and shielding of the metal atom(s) by bulky and inert organic functional groups. The compound should appear to the GC column as a simple organic species and free metal atoms should not be exposed to reactive sites. Inertness of column materials, injection and detection pathways are particularly important. Fused silica columns allow GC of previously inapplicable species. Detectors that are more compatible, selective or specific for inorganic compounds have opened the way for quantitative and sensitive analysis.

Liquid chromatography (LC) has been used extensively in thin-layer and ion exchange for metal ion and compound separations. However high performance column chromatography (HPLC) with different column packings, instrumentation and detectors has given rise to many new capabilities. The literature of LC of inorganics and organometallics up to 1970 was presented by Michal with 700 references while that between 1970 and 1979 was surveyed by Schwedt with over 450 references. MacDonald's (1985) text *Inorganic Chromatographic Analysis* covers all LC and GC methods in a comprehensive review.

The various modes of HPLC allow a wider range of analytes to be chromatographed than in GC. Metal ions may be resolved by ion chromatography, or separated as ion pairs in a reversed-phase regime. Positively or negatively charged metal complexes may be similarly separated. Neutral metal complexes, chelates and organometallics may be chromatographed in reversed- or normal-phase systems. Metal-containing macromolecules such as metalloproteins may be separated by size exclusion. Chemical properties desirable in an inorganic compound for viable liquid partition chromatography include solvolytic stability, minimal adsorptive interactions and shielding of the metal by inert functional groups. As with GC, the analyte should appear to the column as an organic compound and free metal atoms should never be accessible to reactive sites. New detectors that are more compatible or specific for inorganic compounds have also made an impact in HPLC. Diode array UV, electrochemical detection and elemental and molecular mass spectroscopy have proven valuable. The inorganic chromatographer is often faced with a choice between GC and HPLC and each may be valuable in a complementary fashion. Supercritical fluid chromatography (SFC) has been little applied for metal compounds, successful applications following mostly from HPLC methodology.

The primary application of analytical chromatography in metals analysis is clearly in 'speciation' wherein the requirement is resolution and quantitation of specific chemical species incorporating the target metal. Situations occur (i) in which the chemical species is already amenable to the chosen chromatographic technique, and (ii) wherein it may be converted to such by physical or chemical means, as in pyrolysis, derivatization, etc. While total element analysis is less suited to chromatographic methods,

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sometimes suitable derivatization techniques enable this as well.

Gas Chromatography

The classes of metallic substances for which GC is viable, either directly or by derivatization, are: binary metal and metalloid compounds such as halides, hydrides and oxides; sigma-bonded organometallic and organometalloid compounds such as alkyls and aryls; pi-bonded organometallics such as metal carbonyls and metallocenes; chelated metal complexes having nitrogen, oxygen, sulfur, phosphorus, etc., as ligand atoms. The text by Guiochon and Pommier (1973) *Gas Chromatography in Inorganics and Organometallics* provides an excellent summary of this topic augmented by Schwedt's coverage.

Binary Metal and Metalloid Compounds

Binary metal compounds with adequate vapour pressures and thermal stabilities at normal GC temperatures include main group hydrides and halides. At 1000°C or higher, some metal oxides have adequate properties.

Among hydrides, those of boron, silicon, germanium, tin, arsenic, antimony, bismuth, selenium and tellurium are viable having boiling points ranging from 112°C to −2°C. Low column temperatures and inert systems are needed. Element-selective spectral detectors are also advantageous. These separations are important for trace-level determinations in electronic grade organometallics. Organo-hydrides are also readily chromatographed. Analysis of environmentally significant arsenic and antimony compounds with microwave plasma emission detection involves reduction of alkylarsonic acids with sodium borohydride to alkylarsines.

Certain metal halides are sufficiently volatile for GC, but difficulty lies in their high reactivity in the vapour and condensed phases, necessitating precautions to ensure maximum inertness of the system. Among chlorides that have been gas chromatographed are those of titanium, aluminium, mercury, tin, iron, antimony, germanium, gallium, vanadium, silicon and arsenic. Problems arise from reaction with even methyl silicone oils and thus inert fluorocarbon packings have been favoured for reactive chlorides and oxychlorides including $VOCl_3$, VCl_4, PCl_3 and $AsCl_3$. The less volatile metal bromides are very challenging and high temperature stationary phases such as alkali bromide salts coated on silica are needed. Some metal fluorides have low boiling points, e.g. tungsten (17.5°C), molybdenum (35°C), tellurium (35.5°C), rhenium (47.6°C) and uranium (56.2°C), for which low column temperatures are feasible. The determination of alloys and metal oxides, carbides, etc., after conversion to fluorides by fluorination appears feasible.

One of the most extreme modifications of GC has been in the area of very high temperature GC for metal oxides, hydroxides and oxychlorides. Bachmann employed temperatures as high as 1500°C for the separation of oxides and hydroxides of technetium, rhenium, osmium and iridium. Quartz granules were used as the substrate and oxygen and oxygen/water mixtures as carrier gases with the necessary equipment modifications.

Organometallic Compounds

Crompton in *Gas Chromatography of Organometallic Compounds*, published in 1982, notes that during the preceding decade more than 1000 papers were published on this topic, relating to compounds of more than 50 elements. At least as many papers have been published since that time.

Sigma-bonded compounds GC is feasible for compounds of Al, Ga and In from Group III; Ge, Sn and Pb from Group IV; P, As, Sb and Bi from Group V; and Se and Te from Group VI. Also included are Hg and possibly Zn and Cd. The elements that have attracted most analytical interest have been silicon and lead, tin and mercury.

The organic functionalities are typically alkyl, aryl and substituted aryl groups; perfluoroalkyl and aryl groups, which typically impart enhanced volatility; and mixed alkyl-chloro and aryl-chloro systems. The two reported separations of aluminium alkyls leave doubts as to possible on-column decomposition. Trimethylgallium has been eluted along with $(CH_3)_2$ GaCl and CH_3GaCl_2, but no GC of organometallic indium or thallium compounds has been reported. The GC characteristics of alkyl germanium, tin and lead compounds resemble those of silicon but with decreasing thermal stability. For alkylstannanes, on-column oxidation, hydrolysis or thermal degradation must be avoided. Selective detection has been widely used for organotin compounds, notably for environmental samples such as bis(tributyltin)oxide (TBTO) in marine paints, triphenylhydroxystannane pesticide after derivatization to triphenylmethylstannane, and tricyclohexylhydroxystannane in apple leaves after derivatization to tricyclohexylbromostannane.

GC of tetraalkyllead compounds is extensive and covers 30 years of developments. Crompton devotes 90 pages to discussion of organolead GC. The electron-capture detector is highly selective for tetraalkyllleads, but is prone to contamination. Atomic spectral detection has been widely applied for lead-specific

detection, e.g. flame photometric detection with an oxygen–hydrogen flame at 405.8 nm and graphite furnace electrothermal atomic absorption detection at 283.3 nm. Chau quantitated methylethylleads in water, sediment and fish in an investigation of bioalkylation processes, lead detection limits being between 0.01 and 0.025 $\mu g\,g^{-1}$ for solid samples. Plasma atomic emission detection for alkyl leads has been widely used; trimethyl- and triethyllead chlorides have been determined in water in the range of 10 ppb to 10 ppm and also derivatized by butyl Grignard reagent to form the trialkylbutylleads.

The alkyl and aryl derivatives of arsenic and antimony are more labile than those of Group IV elements, and require stringent GC conditions for successful elution. Bismuth compounds have not been chromatographed. Talmi determined As^{3+} and Sb^{3+} in environmental samples as triphenylarsine and triphenylstilbene, plasma emission detection giving limits of 20 pg and 50 pg, respectively.

GC of the environmentally significant organomercurials has attracted much attention, biomethylation of inorganic mercury being important. $(CH_3)_2Hg$ and CH_3HgCl have been separated on packed glass columns using plasma emission detection. Non-flame 'cold vapour', atomic absorption spectrophotometry detection has proved useful after catalytic conversion of organomercurials to elemental mercury.

Although they are not formally organometallics, many alkoxides share similar GC characteristics with alkyl compounds. Germanium, tin, titanium, zirconium and hafnium form stable volatile alkoxides, as do some Group III elements, notably aluminium. There have been GC separations reported of oxycarboxylate salts of beryllium and zinc.

Pi-bonded compounds The most gas chromatographed transition metal organometallics are those containing carbonyl, arene and cyclopentadienyl ligand moieties. Their elution characteristics are very favourable with only rare on-column degradation or adsorption reported. Effective separation of $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ is possible and methods may be employed for the highly toxic $Ni(CO)_4$ since its high volatility permits ready elution. Many results have been reported for arene, cyclopentadienyl and related derivatives of metal carbonyls. Arenechromiumtricarbonyls and molybdenumtricarbonyls are easily gas chromatographed. Cyclopentadienylmanganesetricarbonyl ($C_5H_5Mn(CO)_3$) and its derivatives are well suited to quantitative GC. Methylcyclopentadienylmanganesetricarbonyl, ($CH_3C_5H_4Mn(CO)_3$)-MMT) has been determined in gasoline using various detectors. Capillary GC is effective for compounds of this class; specific element detection simplifies such separations and provides qualitative and quantitative proof of elution. **Figure 1** shows such a capillary column separation with atomic emission detection of organometallics with differing metals and functionalities. Many of these organometallics are of interest as polymerization catalysts, etc.

Among GC of metallocenes, ferrocene, bis(cyclopentadienyl)iron, is the most familiar example. These compounds have favourable GC properties, ferrocene proving an ideal organometallic probe for determining column and system efficiency. Ferrocene derivatives chromatographed have included alkyl, vinyl, dialkyl, acetyl, diacetyl and hydroxymethyl compounds. GC behaviour is determined largely by the substituents; ruthenocene and osmocene have also been separated.

Metal Chelates

Neutral metal complexes deriving from a number of anionic ligands with oxygen, nitrogen, sulfur or phosphorus donor atoms, have been widely studied. The range of organic ligands that has been shown to be suitable for GC analysis has been limited, but a considerable amount of development and application has been done.

Beta-diketonates Beta-diketonates are readily formed with stability arising from multiple chelate rings. Ions with coordination numbers twice their oxidation state such as Al(III), Be(II) and Cr(III) form coordinatively saturated neutral complexes which are good for GC but the non-fluorinated beta-diketonates are generally of marginal thermal and chromatographic stability; they usually require column temperatures too high for thermal degradation to be completely absent. The major breakthrough in metal chelate GC involved fluorinated beta-diketone ligands, giving complexes of greater volatility and thermal stability. Moshier and Sievers gave the major impetus to this development, and a major portion of their monograph summarizes the analytical progress made to that time. Trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione-HTFA) and hexafluoroacetylacetone (1,1,1,5,5,5-hexafluoro-2,4-pentanedione-HHFA) have been the most widely studied and analytically developed of the fluorinated beta-diketonates. HTFA extended the range of metals that may be quantitated to include Ga(III), In(III), Sc(III), Rh(III) and V(IV). HTFA chelates of trivalent hexacoordinate metals such as Cr(III), Co(III), Al(III) and Fe(III) exhibit geometrical isomerism with facial (*cis*) and meridonal (*trans*) forms present and interconverting. Numerous analytical applications of HTFA chelates are reviewed in detail by Moshier and

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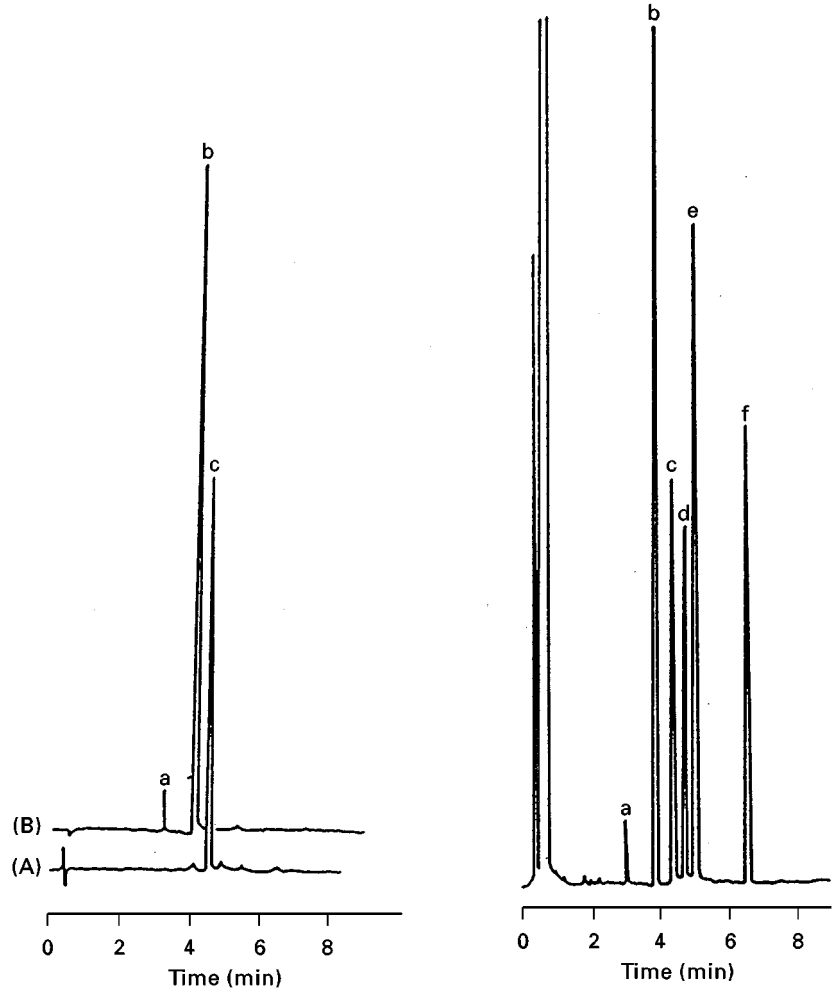


Figure 1 Microwave plasma atomic emission capillary GC detection of organometallics. Left: (A) chromium monitored at 267.7 nm (peak c) and (B) manganese monitored at 257.6 nm (peaks a and b). Right: carbon monitored at 247.9 nm for organometallic mixture. The six peaks afford 'universal' carbon detection. The identities of the eluted peaks are: (a) $C_5H_5Mn(CO)_3$, (b) $CH_3C_5H_4Mn(CO)_3$, (c) $C_5H_5Cr(NO)(CO)_2$ and $(C_5H_5)_2Ni$ (unresolved), (d) $C_5H_5V(CO)_4$, (e) $(C_5H_5)_2Fe$ and (f) $C_5H_5(CH_3)_5Co(CO)_2$. (Reproduced with permission from Estes SA *et al.* (1980). *Journal of Chromatography and Chromatographic Communications* 3: 471. Copyright John Wiley & Sons Ltd.)

Sievers, Uden and Henderson and in the texts of Guiochon and Pommier and Schwedt.

Since modifications of the beta-diketone structure may be made readily, various such ligands have been evaluated for GC. The two major adaptations have been the replacement of the methyl group by higher branched alkyl groups, notably *t*-butyl, and the incorporation of longer chain perfluoroalkyl groups in the ligand. Sievers used 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (heptafluoropropanoylpivalylmethane (HFOD or HHPM)) for lanthanide separations.

Alternative beta-difunctional chelates The major classes of such ligands are summarized in the schematic diagram in **Figure 2**. This indicates the mode of formation of the main alternative bidentate ligands with sulfur donors and bidentate and tetradentate ligands with nitrogen donors.

Beta-thioketonates There are a number of advantages of these chelates. The metals showing favourable GC properties are those whose diketonates are generally unsatisfactory, such as the divalent metals nickel, palladium, platinum, zinc and cobalt. Nickel has been subjected to a complete quantitative analysis, as the monothiotrifluoroacetylacetonate.

Beta-ketoaminates The presence of the nitrogen atom in the ligand dictates an intermediate place between beta-diketonates and monothioketonates in terms of the metals which are readily complexed. The nickel group of metals is favourably complexed, but in addition stable chelates of copper(II) are formed,

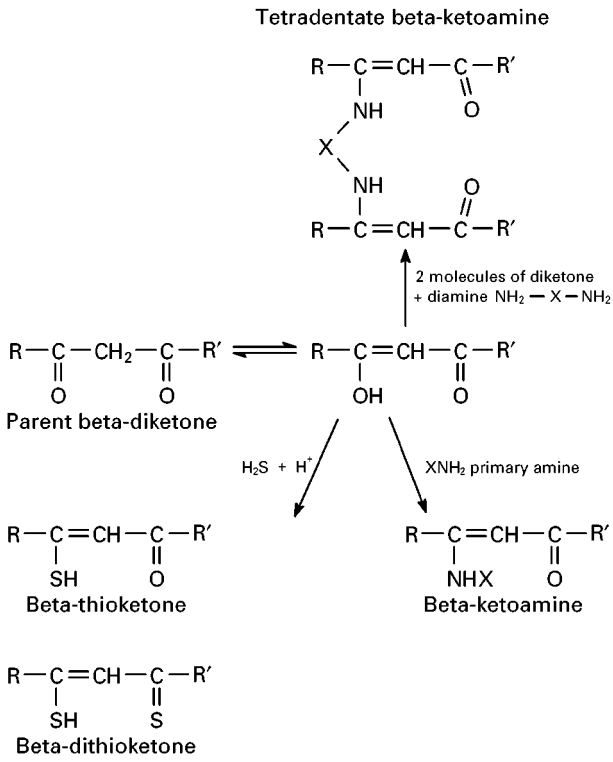
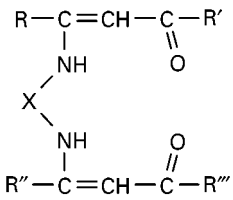


Figure 2 Formation of beta-difunctional ligands for metal gas chelate gas chromatography. (Reproduced with permission from Estes SA *et al.* (1980). *Journal of Chromatography and Chromatographic Communications* 3: 471. Copyright John Wiley & Sons Ltd.)

as are those of vanadyl (V(IV)O). The bidentate ketoamines are of only marginal GC stability to submicrogram elution level, but tetradentate beta-ketoamine ligands form a useful group for GC of divalent transition metals. The addition of the extra five-membered ring stabilizes the complexes, which more than offsets their lowered volatility. **Table 1** lists the tetradentate beta-ketoamine ligands that have been evaluated for GC of copper, nickel, palladium and vanadyl complexes. The fluorinated chelates have very great electron capturing abilities affording picogram level detection.

Table 1 Representative tetradentate beta-ketoamine ligands used for chelate formation and gas chromatography of divalent transition metals



R	*R′*	*R″*	*R‴*	*X*	*Ligand symbol*
CH_3	CH_3	CH_3	CH_3	en	H_2(enAA$_2$)
CH_3	CH_3	CH_3	CH_3	pn	H_2(pnAA$_2$)
CH_3	CH_3	CH_3	CH_3	bn	H_2(bnAA$_2$)
CF_3	CH_3	CH_3	CF_3	en	H_2(enTFA$_2$)
CF_3	CH_3	CH_3	CF_3	pn	H_2(pnTFA$_2$)
CF_3	CH_3	CH_3	CF_3	bn	H_2(bnTFA$_2$)
$C(CH_3)_3$	CH_3	CH_3	$C(CH_3)_3$	en	H_2(enAPM$_2$)
$C(CH_3)_3$	CH_3	CH_3	$C(CH_3)_3$	pn	H_2(pnAPM$_2$)
CF_3	$C(CH_3)_3$	$C(CH_3)_3$	CF_3	en	H_2(enTPM$_2$)

en = CH_2–CH_2; pn = $CH(CH_3)$–CH_2; bn = $CH(CH_3)$–$CH(CH_3)$.

Dialkyldithiocarbamates and dialkyldithiophosphinates The metals complexed by these ligands are parallel to those chelated by the tetradentate beta-ketoamines for GC applications. Zinc, copper and nickel have been determined in marine bottom sediments and in sea sands and muds. In parallel to the development of fluorinated beta-diketone ligands, fluorinated dialkyldithiocarbamates show analytical promise due to their increased volatility over non-fluorinated analogues. Tavlaridis and Neeb first investigated di(trifluoroethyl)dithiocarbamates, eluting zinc, nickel, cadmium, lead, antimony and bismuth complexes at 185°C. Sucre and Jennings reported effective capillary separation of these complexes of nickel and cobalt(III) on 5 metre fused silica columns. It appears likely that further refinement of high resolution columns will broaden the application of these versatile complexes for analytical GC.

Cardwell and McDonagh separated zinc, nickel, palladium and platinum 0,0′-dialkyldithiophosphinates. These complexes are suitable for selective detection by flame photometry with monitoring of either the S_2 or HPO emission modes.

Metalloporphyrins One of the most important demonstrations of the expanded range of sample applications for inorganic GC brought about by high resolution fused silica capillary was of transition metal porphyrin complexes. Marriott achieved capillary GC elution of these closed macrocylic ring copper, nickel, vanadyl and cobalt aetioporphyrin I, and octaethyl-porphyrin chelates with Kováts indices in the range 5200–5600.

Chromatographic Detection

Of particular value for metal compound chromatography are detectors giving 'selective' or 'specific' information on the eluates. Spectral property detectors such as the mass spectrometer (MS), the infrared spectrophotometer (IRS) and the atomic emission spectrometer (AES) fall into this class. The latter 'element selective' detectors are widely used: the microwave-induced plasma in particular for GC and the inductively coupled plasma mass spectrometer (ICPMS) for HPLC. These detector systems typically

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offer nanogram level detection or lower for metal content of analytes. Metals may be determined directly or through derivatization procedures which render them more readily separable and detectable.

High Performance Liquid Chromatography

Size-Exclusion Chromatography (SEC)

SEC separates chemical species by molecular size and shape in a column containing particles of a rigid packing with a defined pore structure. Many applications to inorganic and organometallic species have been reported ranging in size from a few hundred to 10^5 Da or greater; from labile nickel complexes of alkyl substituted phosphorus esters to molecular clusters of inorganic colloids in the 1–50 μm range, aluminosilicate sols, humic acid metal complexes, metallopeptides and metalloproteins. Ferritin, an iron-containing protein which exists in a number of discrete forms, has been analysed using aqueous SEC, good repeatability being found for iron at the nanogram level. Trace levels of Cd, Zn and Cu metalloproteins in marine mussels were determined using SEC with sequenced UV absorption detection before the ICP. In the petroleum field, effective separation and determination of vanadium and nickel metalloporphyrins has been accomplished. Columns of pore size 10 nm in particular are a viable choice for many separation problems of inorganic chromatography.

Reversed-Phase High Performance Liquid Chromatography (RPHPLC)

RPHPLC of inorganic and organometallics may be characterized by the detector used and some examples are noted.

Atomic absorption (AA) The interfacing of column effluent and an AA spectrometer was attained in 1973, tetraalkyllead compounds being separated on C_{18} μ-Bondapak with 70% acetonitrile and 30% water. The superiority of AA detection over UV detection was shown, since gasoline samples have components that mask the tetraalkyl lead compounds.

Inductively coupled plasma (ICP) and direct current plasma (DCP) Plasma spectral detection for HPLC has emphasized the ICP and to some extent the DCP, in contrast to the dominance of the microwave-induced plasmas as element-selective GC detectors. Metal-specific detection is predominant and will probably remain so until more eluate-selective interface systems can be devised. The ICP became commercially available in 1974 replacing atomic absorption spectroscopy as the method of choice for metal analysis. The technique and DCP has been coupled to HPLC for trace analysis and speciation of real-world samples such as arsenite, dimethyl arsenate and arsenate. A 130 ng mL^{-1} detection limit for arsenic in organoarsenic acids was found for 100 μL samples after hydride formation. Separation of mercury cations employed an alkyl sulfonate anion as ion pair reagent and, after hydride formation, gave detection limits of 50–100 μg L^{-1}. A possible solution to overcome the difficulties in quantitative transfer of HPLC eluate involves a total injection microconcentric nebulizer (DIN) which can achieve almost 100% nebulization and transport efficiency. Detection limits down to 4 mg L^{-1} for zinc have been reported. The DCP gave detection for Cr(III) and Cr(VI) linear over at least three orders of magnitude with a detection limit of 10 μg L^{-1}; applications include biological samples from ocean floor drillings, chemical dump sites, surface well water and waste water samples.

Visible and UV detection Spectrophotometric complexing reagents are widely used for visible spectral determination of many metals at low concentrations, but these complexes are seldom suited to HPLC. Pyridylazonaphthol complexes of copper, nickel and cobalt are separable by reversed-phase LC using acetonitrile/water/citrate buffer at pH 5 (80 : 18 : 2), 0.01 mol L^{-1} ammonium thiocyanate, and other such stable chelates are also amenable. In addition, non-absorbing species may be detected after conversion to chromophores by complexing, ion pairing or other chemical reactions. Neutral metal chelates such as beta-diketonates, beta-ketoaminates, dialkyldithiocarbamates and dialkyldithiophosphinates separable by GC may also be chromatographed by reversed-phase HPLC and less volatile complexes are also amenable to the technique.

Amperometric and differential pulse detection Dithiocarbamates of Cu(II), Ni(II), Co(II), Cr(III) and Cr(VI) have been detected amperometrically after HPLC separation. Although both the oxidation and reduction reactions of these organometallics are well defined, the ubiquitous presence of reducible oxygen dissolved in the polar solvent results in the oxidative process being more desirable. Knowledge of solvent, electrodes and electrochemistry is essential before a correct HPLC-EC protocol can be stated. Cancer chemotherapeutic drugs cisplatin, mitocynin C and mitoxanthrone are separable on C_{18} columns and are easily detected by oxidation, if the cisplatin oxidation

potential is shifted by 0.10 mol L^{-1} chloride to 0.80 V.

Detection selectivity may be improved by differential pulse detection as in the reversed-phase determination of alkyl- and aryl-mercurials, tri-*n*-butyl tin, triethyl tin and triphenyl tin.

Ion Pair Chromatography (IPC)

Combination of ion exchange and partition mechanisms and the performance of 5 and 10 μm C_{18} silica bonded phases give high performance ion separation in the direct and ion-paired modes. Pairing ions may be present in the mobile phase or retained on the surface. A C_{18} column coated with C_{20} alkyl sulfate gave baseline separation of Cu(II), Co(II) and Mn(II). The eluted metal ions were detected by absorption spectrophotometry at 530–540 nm after post-column reaction with 4-(2-pyridylazo)-resorcinol (PAR). Paired-ion HPLC separation of iron(II), nickel(II) and ruthenium as cationic 1,10-phenanthroline complexes with alkylsulfonic acids was achieved. Crown ethers can form stable complexes with metal cations, reversed-phase HPLC retention being dependent upon the relative size of the cation and the ring of crown ether. A typical elution order is $Li^+ < Na^+ < Cs^+ < Rb^+ < K^+$, and $Mg^{2+} Ca^{2+} < Sr^{2+} < Ba^{2+}$.

Overall, the choice in inorganic column liquid chromatography is now between reversed-phase, including paired-ion, and ion chromatography, the former typically affording the better resolution.

HPLC-ICP-Mass Spectrometry (HPLC-ICP-MS)

The most extensively developed plasma mass spectral analytical technique is that of ICP-MS. The argon ICP acts as a mass spectral ion source; for a sample solution, after aerosol formation in a nebulizer and spray chamber, analyte is injected into the plasma where it undergoes desolvation, vaporization, atomization and ionization. A portion of the ions is sampled from the centre of the plasma and directed, through a low pressure interface, into the mass spectrometer. ICP-MS combines advantages of ICP-AES such as multi-element analysis, wide dynamic range and speed, with mass spectral acquisition, enhanced detection limits (typically 0.01–0.1 mg L^{-1}) and capability for isotopic analysis. In HPLC-ICP-MS detection limits as low as 100 pg/peak have been obtained for many elements. Ion exchange and ion pair chromatography were used for speciation of triorganotin species and arsenic speciation has been examined in a number of studies. The technique shows excellent prospects in biomedical and clinical studies in which analyte levels are usually below the capabilities of ICP emission detection. Interfaced aqueous SEC with ICP-MS was used for element and isotope ratio detection of lead and copper in protein fractions of serum and blood cell haemolysate with molecular weight ranges from 11 kDa to > 600 kDa and detection limits in the 1–10 μg L^{-1} range for metallodrugs and their metabolites, measured in samples from patients undergoing gold drug therapy for arthritis. The elements mercury, arsenic, lead and tin have attracted most interest from the trace element environmental point of view.

Conclusions

High performance gas and liquid chromatography of metal compounds have always presented considerable challenges, but have in return provided many analytical and characterization insights, both qualitative and quantitative. In practical terms, the wider adoption of element-specific spectral detection depends on the continual development of commercial instrumentation to permit inter-laboratory comparisons of data and the development of 'recommended' methods of analysis which can be widely used. Many areas of analysis are subject to restrictions designed to ensure high levels of accuracy and precision. Fully integrated units which remove the need for analysts to interface their own GC, emission device and spectrometer may become as familiar in the future as GC-MS and GC-FTIR systems are today. Integrated HPLC and SFC systems will be longer delayed, but their eventual adoption is inevitable in view of the broad scope of these separation methods.

See also: **II / Chromatography: Gas:** Detectors: General (Flame Ionization Detectors and Thermal Conductivity Detectors); Detectors: Mass Spectrometry; Gas Chromatography-Infrared; Gas-Solid Gas Chromatography; Historical Development. **Chromatography: Liquid:** Detectors: Mass Spectrometry.

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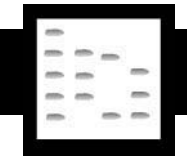
METAL COMPLEXES



Ion Chromatography

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Introduction

Many different and clever methods have been reported in the literature for the separation of metal ions. Most involve chemical reactions in which complexes are formed between the hydrated metal ions and an inorganic or organic ligand. If an organic ligand is employed coordination is usually through oxygen, sulfur or nitrogen atoms, individually or in combination.

In a simplified representation the stepwise and overall formation of metal–ligand complexes can be represented by the following:

$$M^{2+} + HL = ML^{+} + H^{+} \quad [1]$$

$$ML^{+} + HL = ML_2 + H^{+} \quad [2]$$

$$M^{2+} + nHL = ML_n^{+2-n} + nH^{+} \quad [3]$$

where M^{2+} is a divalent hydrated cation (acceptor) and HL is a monoprotic weak acid ligand (donor) that replaces the waters of coordination in a series of steps. The formation and dissociation of the metal–ligand (donor–acceptor) complexes proceeds, often rapidly, by a series of equilibrium reactions, each of which is defined by a formation constant. Because of the metal ion coordination number, the stepwise equilibria, the formation constant, and concentrations of the metal ion and ligand, a series of complexes (see the expression of the total equilibrium steps in eqn [3]) may coexist in the solution. When the ligand is neutral the charge of the resulting complexes are positive. However, the complexes may associate with solution anions to produce neutral species. Ligands can also be anions, eqns [1]–[3], and thus the complexes that form can be cations, neutral or anionic, depending on the coordination number of the metal ion, the number of ligands bound to the metal ion, the formation constants for the complexes that form, and the metal ion and anionic ligand concentrations.

Conversion of a metal analyte into a complex is important in separations for two major reasons. First, the chemical and physical properties of the metal–ligand complex are sharply different than those of the metal ion hydrate. Solubility, ionic or polar character, and even volatility can be different. Formation constants for the metal–ligand complexes will differ and pH is often an important variable. Thus, the number of separation strategies that are applicable to the separation of metal ions are broadened and the number of variables that can be altered to bring about resolution in the separation of a complex mixture of metal ions is increased. Second, some metal–ligand complexes can be more easily detected, which improves quantitative estimation and even identification, than the metal ion hydrate. For example, metal–ligand complexes can be highly coloured, while some will fluoresce and/or have electrochemical properties that can be monitored.

Using complex formation between a ligand and metal ion to facilitate metal ion separations was an important strategy in the development of low efficiency liquid column chromatographic separations of metal ions, particularly in separations by ion exchange and partition column chromatography. Similarly, complex formation is a key elution parameter in high efficiency liquid column chromatographic separations. Each of these column strategies is briefly described in the following.

Ion Exchange

In ion exchange column chromatography the column is packed with either a cation exchanger, which will